Supplementary Information

Bis(alkyl)thioethers on a biphenyl scaffold: A spectroscopic and structural insight

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Contents

1. Figures

1.1 Figure S1 – Full mass spectrum of desired tellurium product

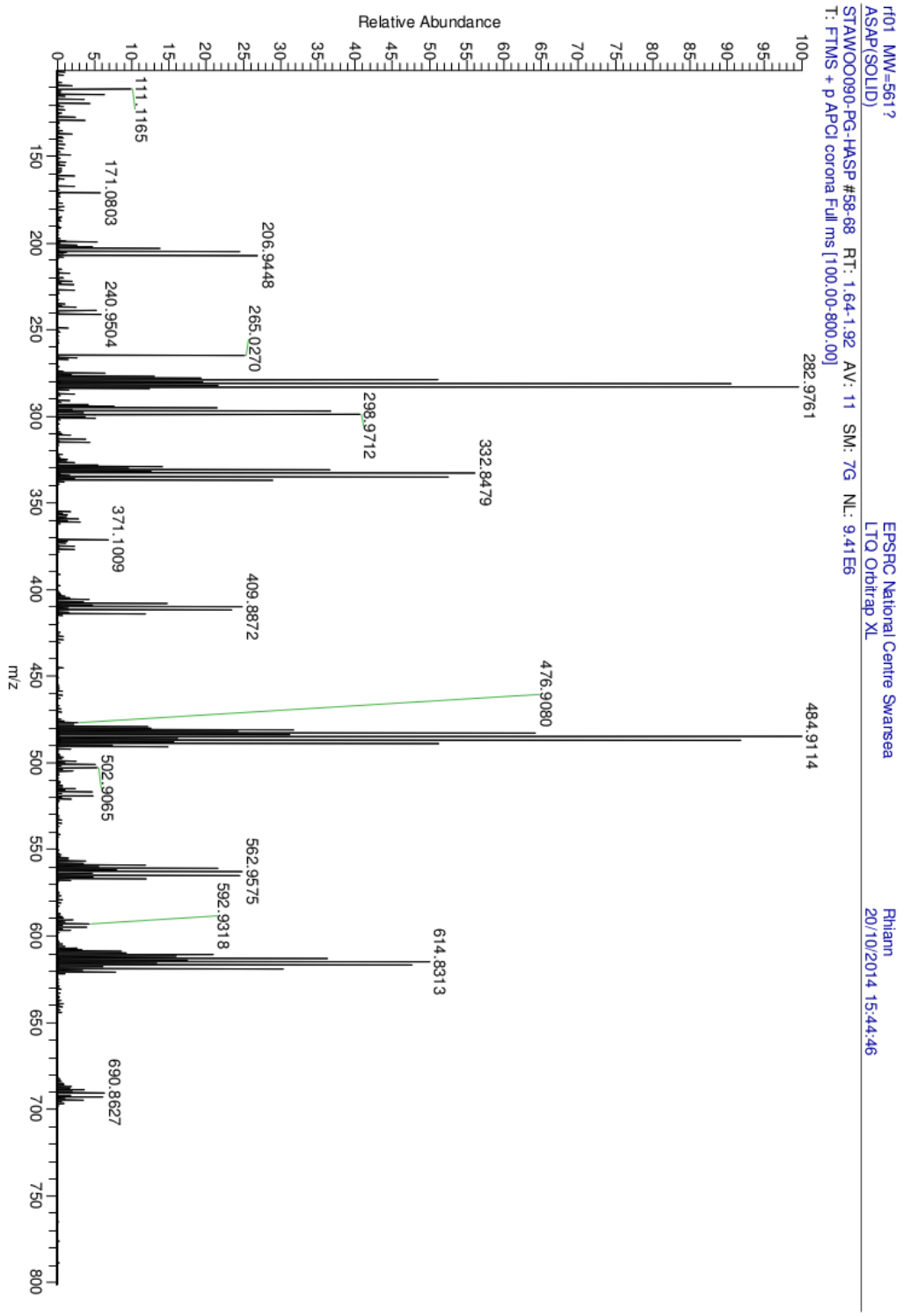


Figure S1: Mass spectrum containing signal for desired tellurium compound at *m/z* 562.9575.

1.2 Figure S2 – Isotopic distribution pattern of desired tellurium product

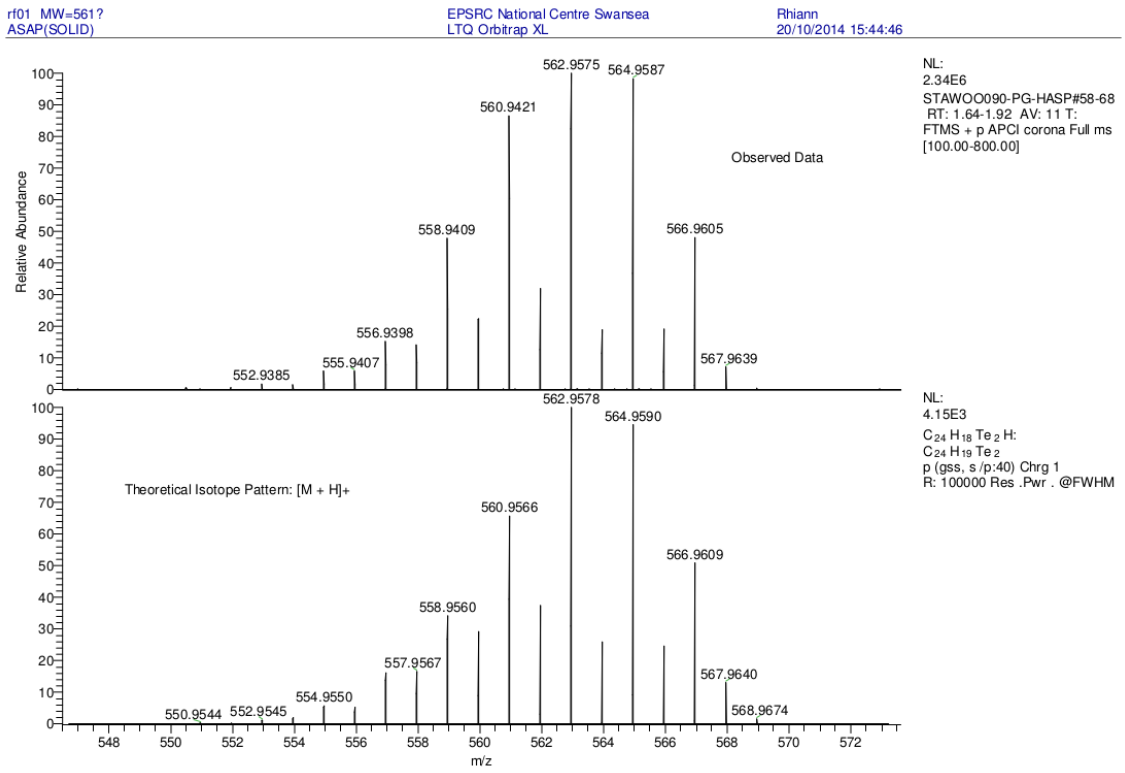


Figure S2: Isotopic distribution pattern (observed (top) and theoretical (bottom)) for desired $[M+H]^+$ signal from the tellurium compound.

1.3 Figure S3 – NMR data for compound 4

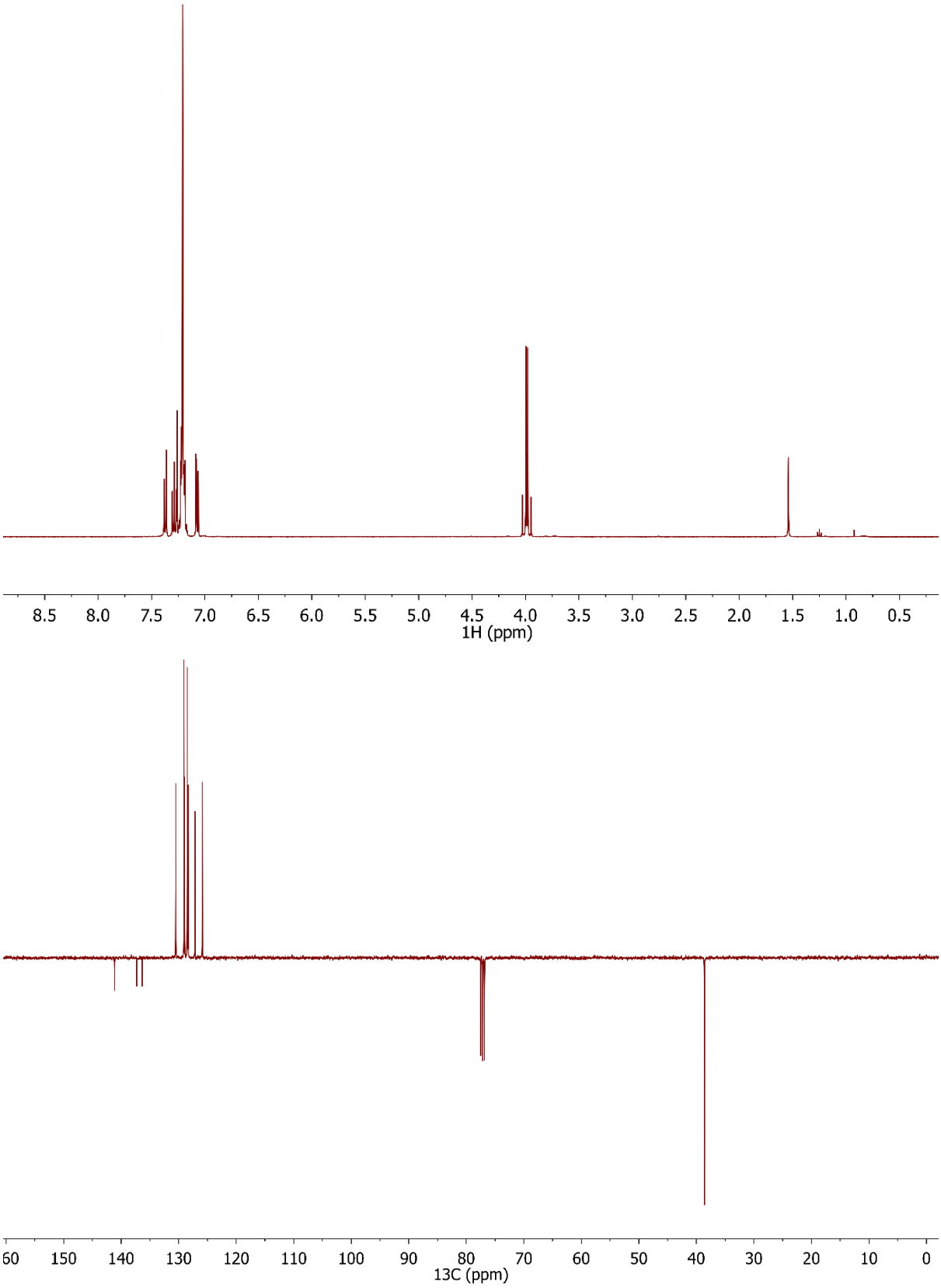


Figure S3: ^{1}H (400.1 MHz, $CDCl_3$, 295 K) (top) and $^{13}C\{^{1}H\}$ DEPT-Q (100.6 MHz, $CDCl_3$, 295 K) (bottom) NMR spectra for compound **4**.

1.4 Figure S4 – NMR data for compound 5

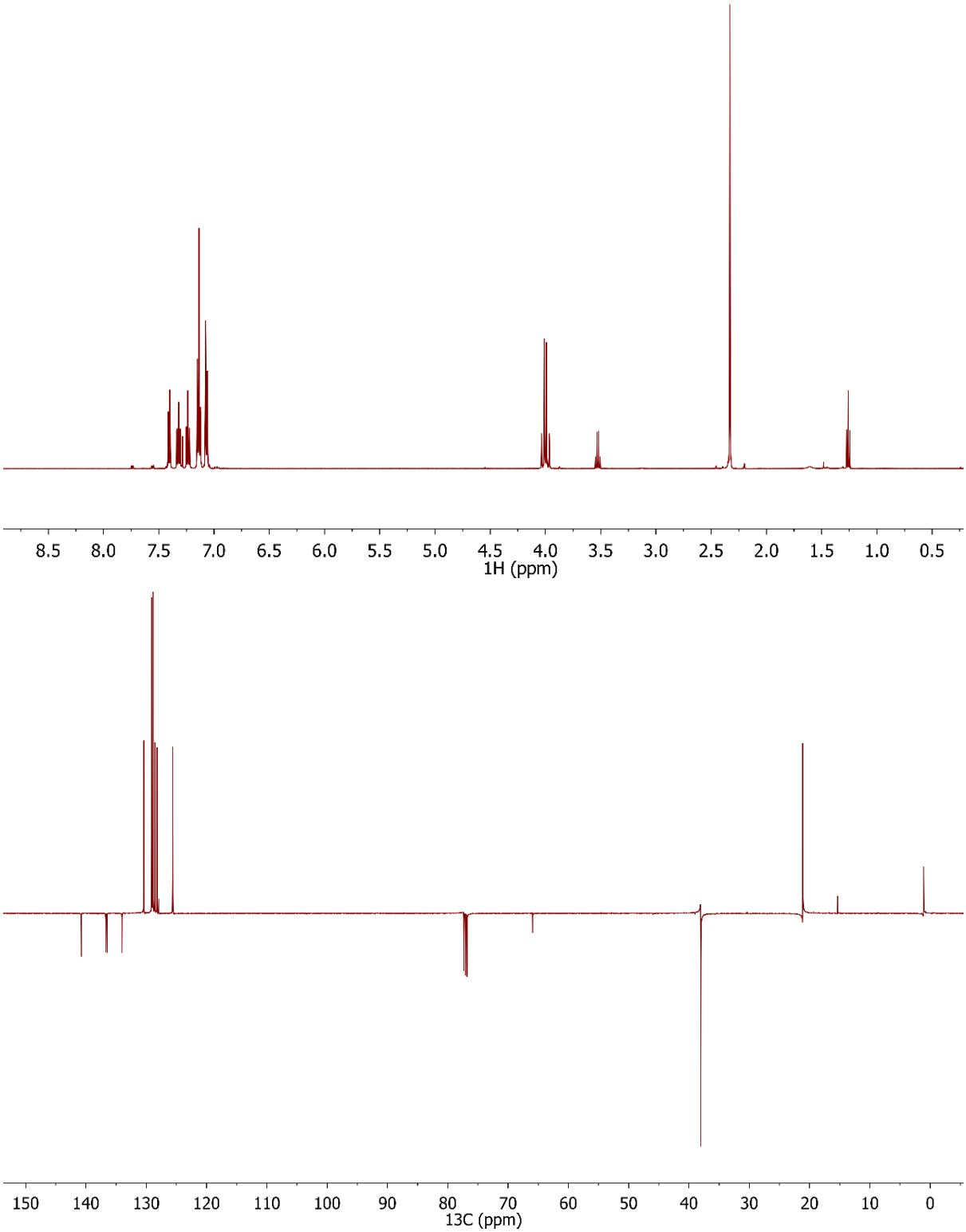


Figure S4: ^{1}H (500.1 MHz, $CDCl_3$, 295 K)(top) and $^{13}C\{^{1}H\}$ DEPT-Q (125.8 MHz, $CDCl_3$, 295 K) (bottom) NMR spectra for compound **5**.

1.5 Figure S5 – NMR data for compound 6

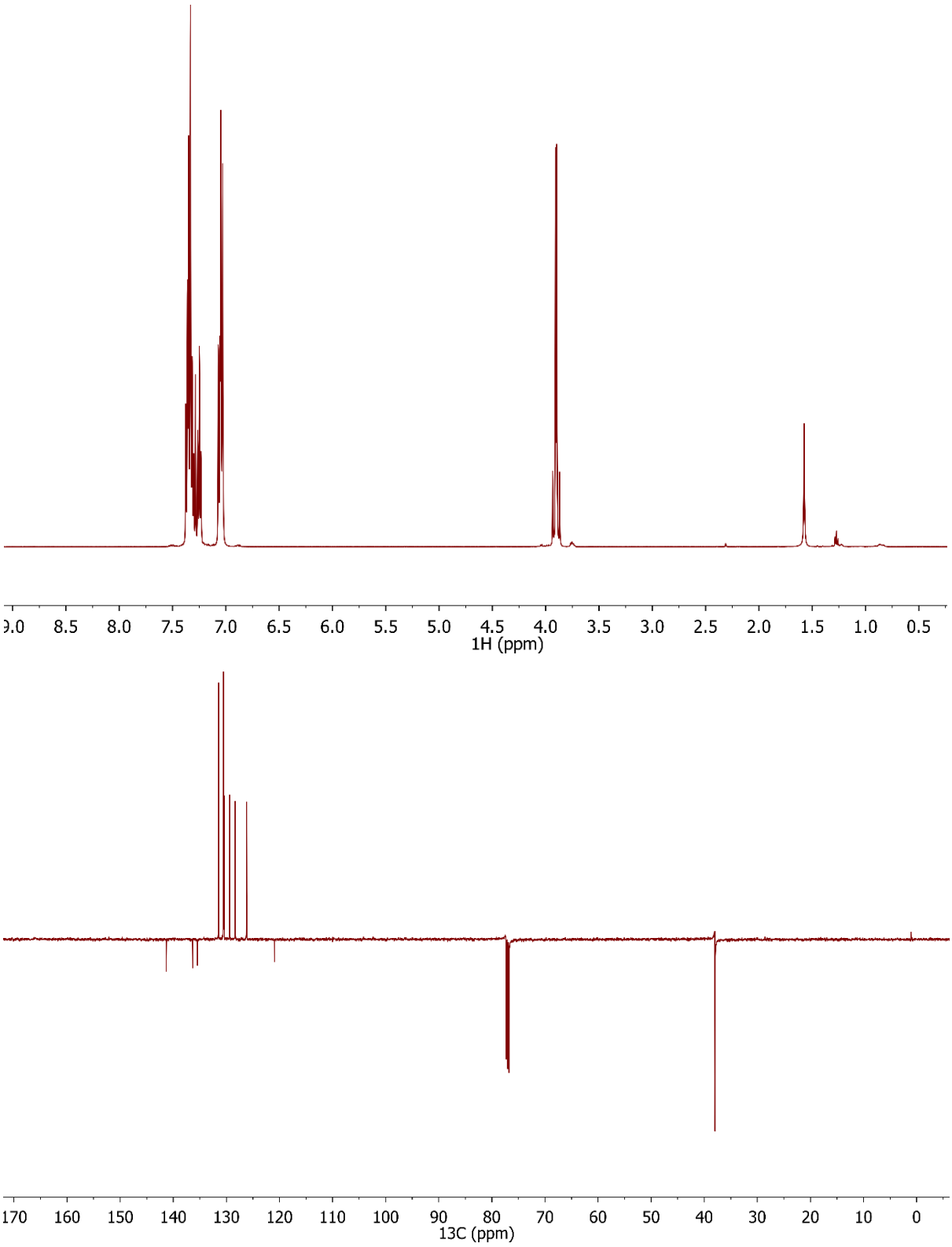
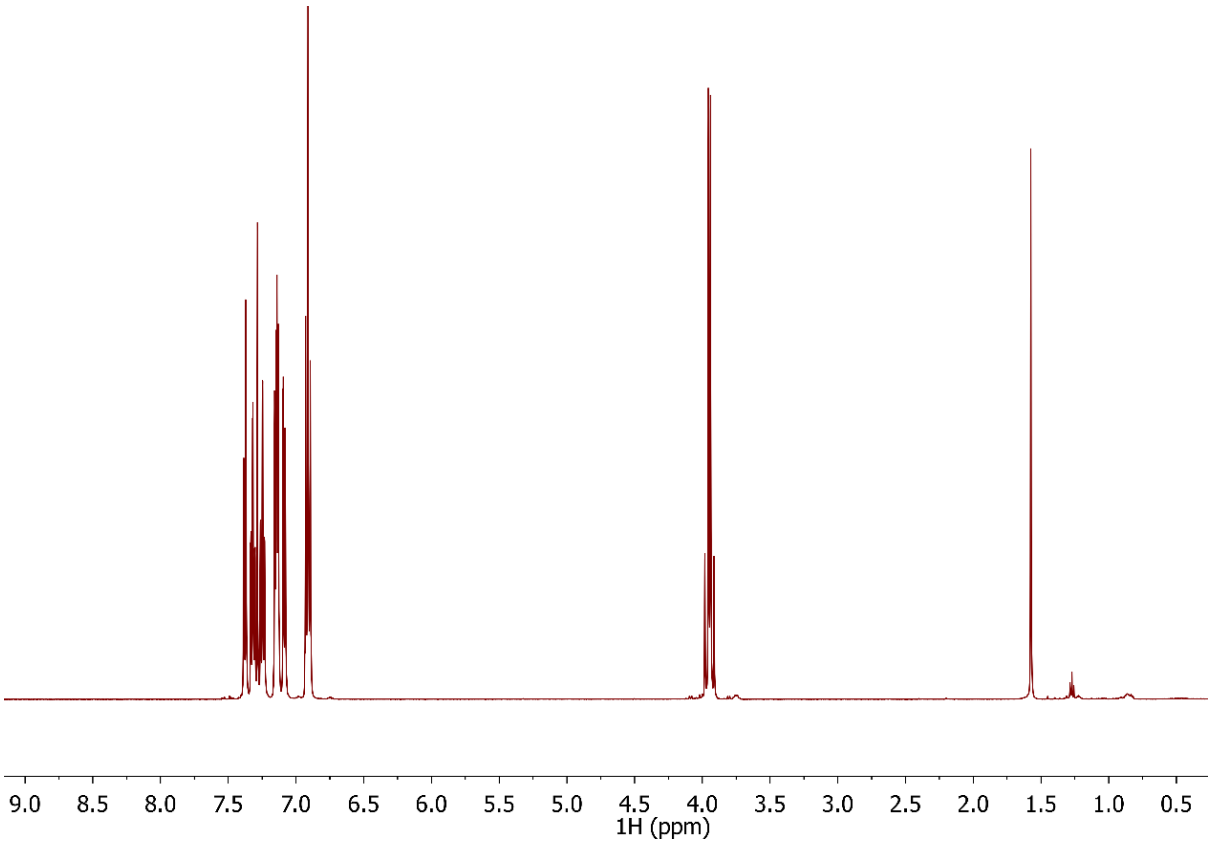
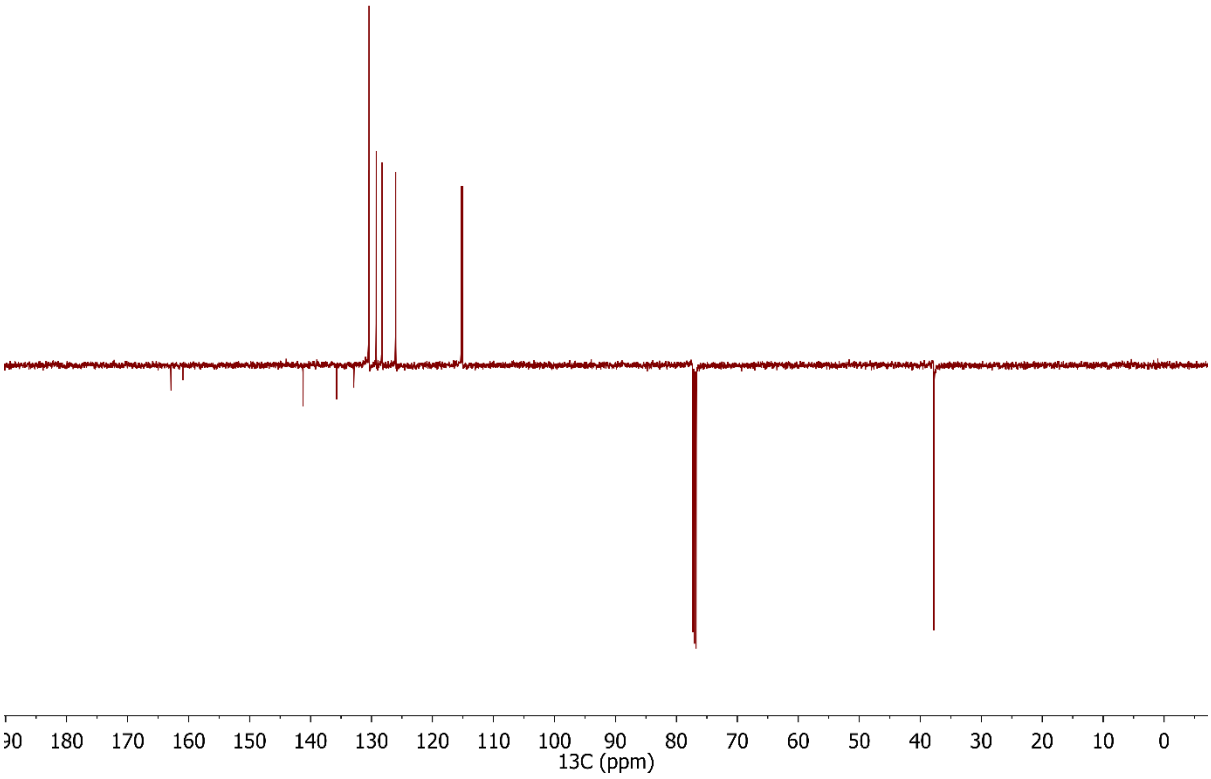


Figure S5: ^{1}H (500.1 MHz, $CDCl_3$, 295 K) (top) and $^{13}C\{^{1}H\}$ DEPT-Q (125.8 MHz, $CDCl_3$, 295 K) (bottom) NMR spectra for compound **6**.

1.6 Figure S6 – NMR data for compound 7





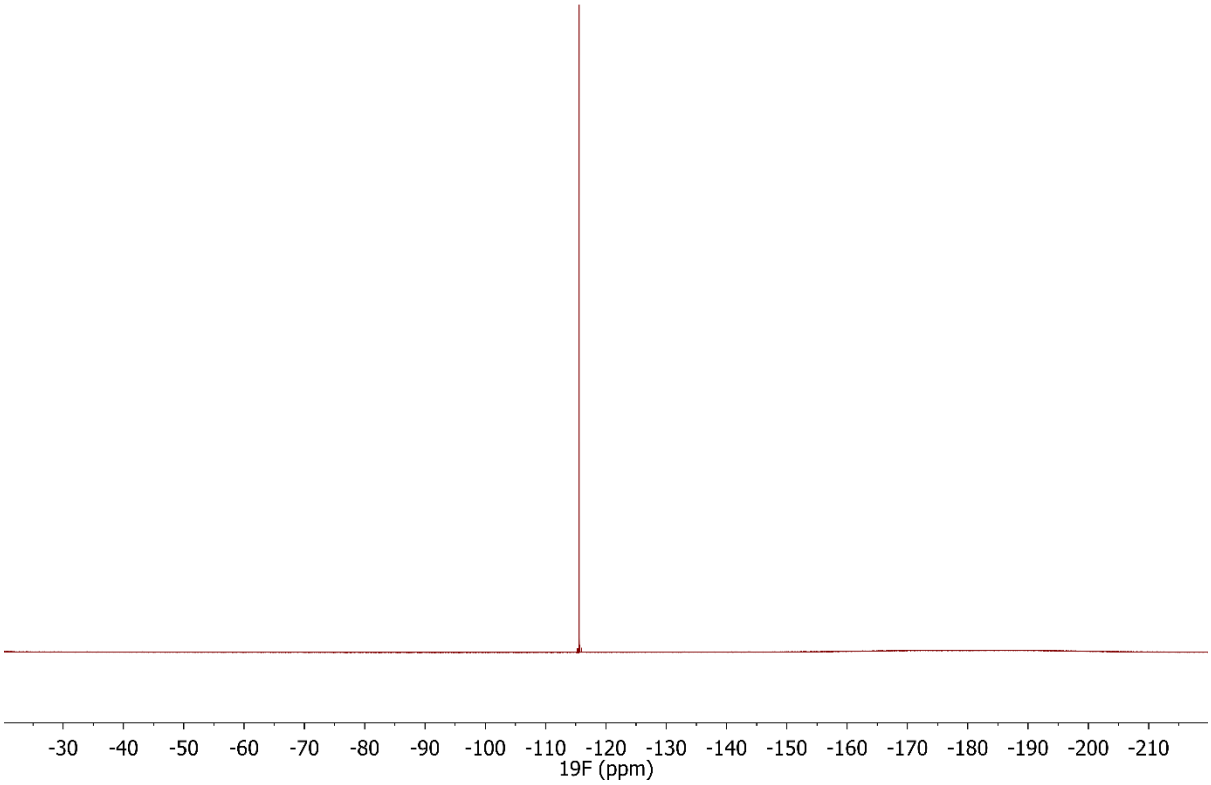
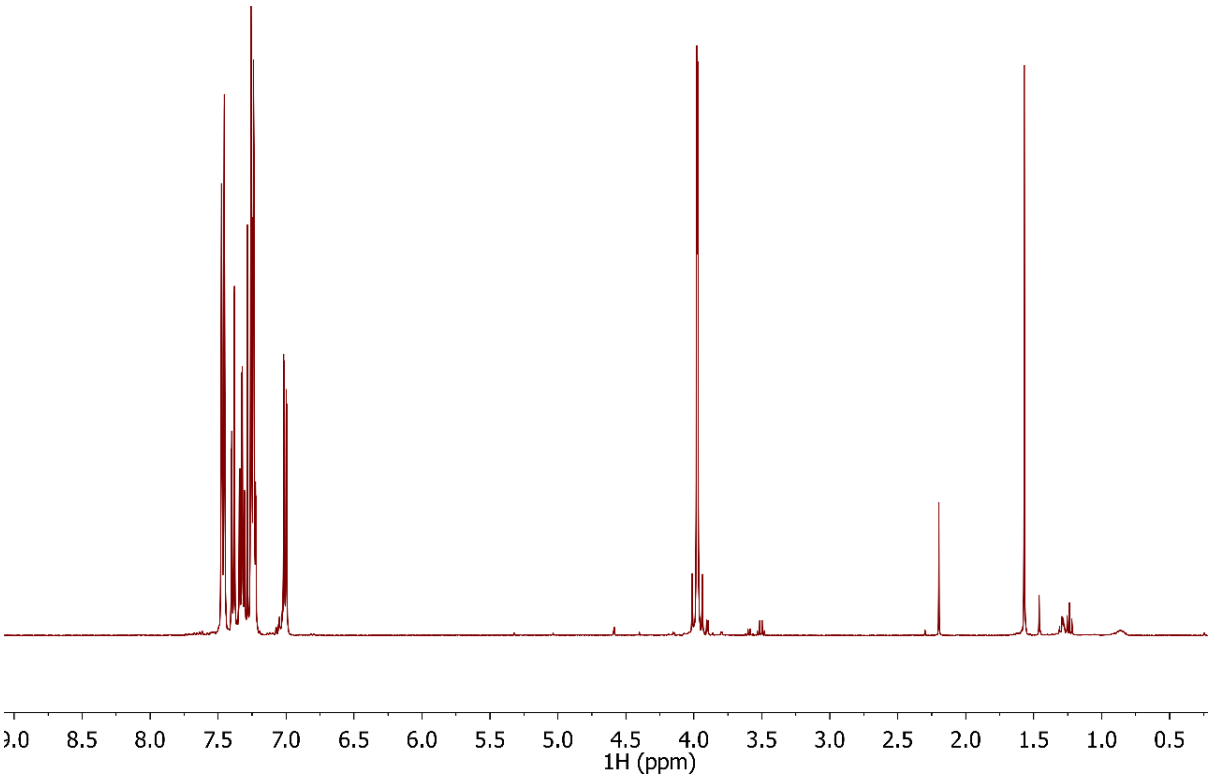
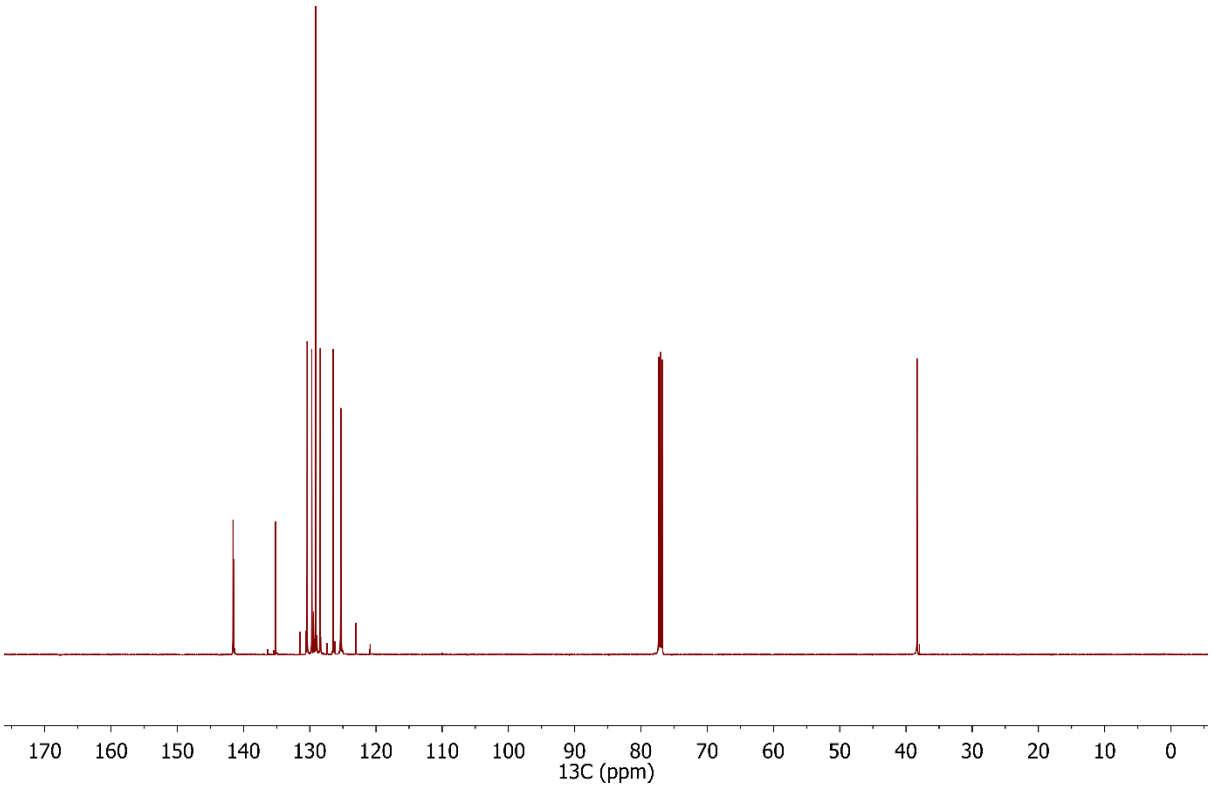


Figure S6: ^{1}H (500.1 MHz, $CDCl_3$, 295 K) (top), $^{13}C\{^{1}H\}$ DEPT-Q (125.8 MHz, $CDCl_3$, 295 K) (middle) and $^{19}F\{^{1}H\}$ (376.5 MHz, $CDCl_3$, 295 K) (bottom) NMR spectra for compound **7**.

1.7 Figure S7 – NMR data for compound 8





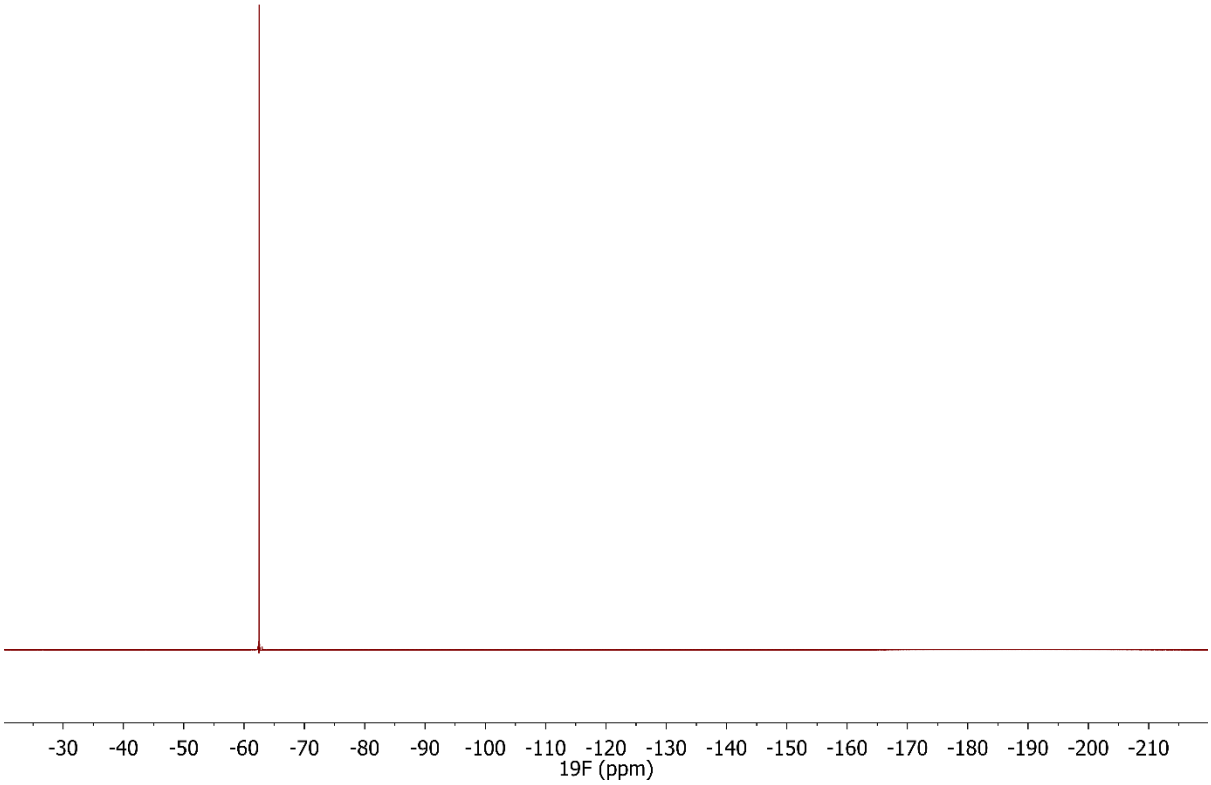


Figure S7: ^{1}H (400.1 MHz, $CDCl_3$, 295 K) (top), $^{13}C\{^{1}H\}$ (100.6 MHz, $CDCl_3$, 295 K) (middle) and $^{19}F\{^{1}H\}$ (376.5 MHz, $CDCl_3$, 295 K) (bottom) NMR spectra for compound **8**.

1.8 Figure S8 – NMR data for compound 9

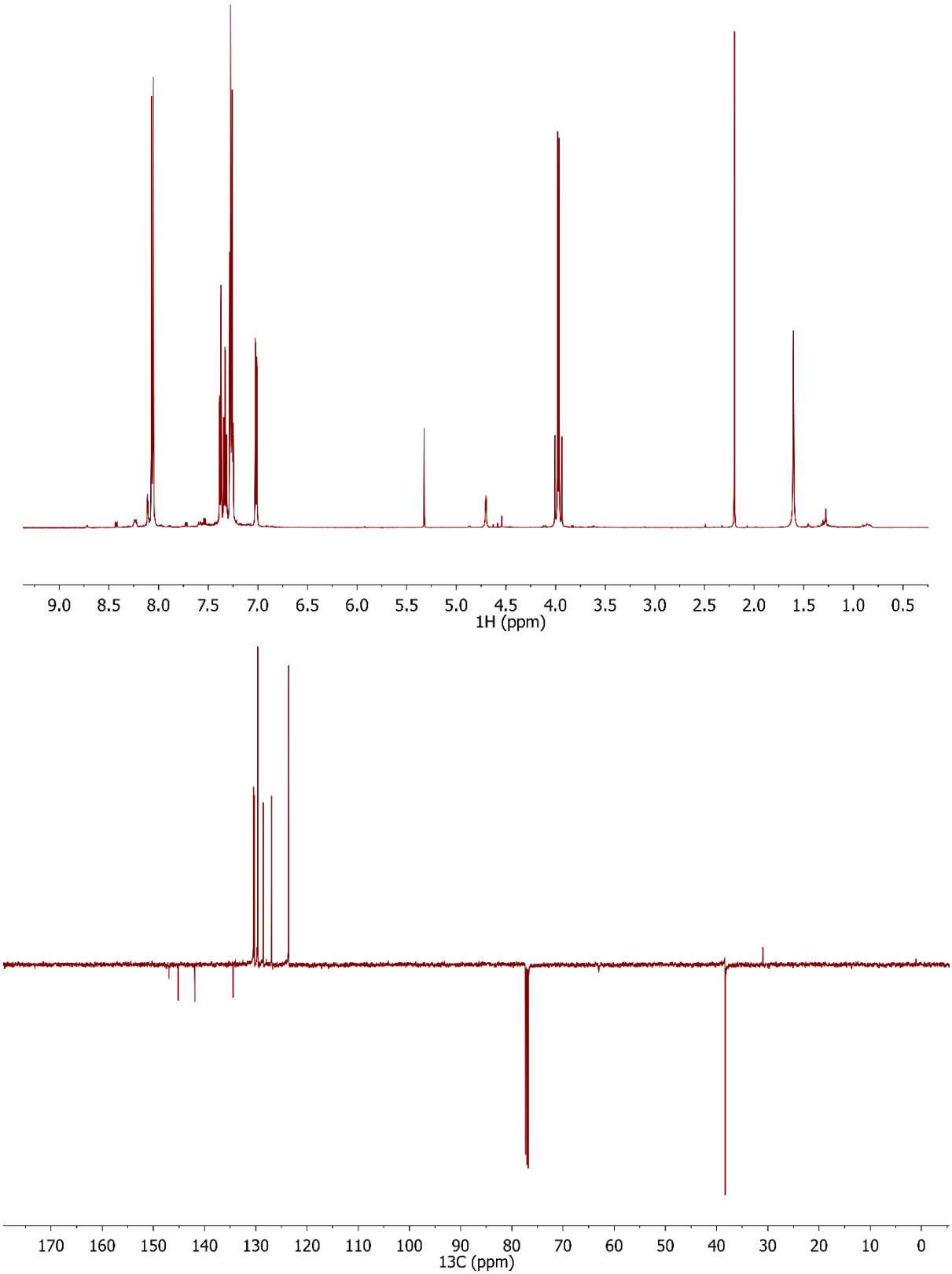


Figure S8: ^{1}H (500.1 MHz, $CDCl_3$, 295 K) (top) and $^{13}C\{^{1}H\}$ DEPT-Q (125.8 MHz, $CDCl_3$, 295 K) (bottom) NMR spectra for compound **9**.

1.9 Figure S9 – NMR data for compound 10

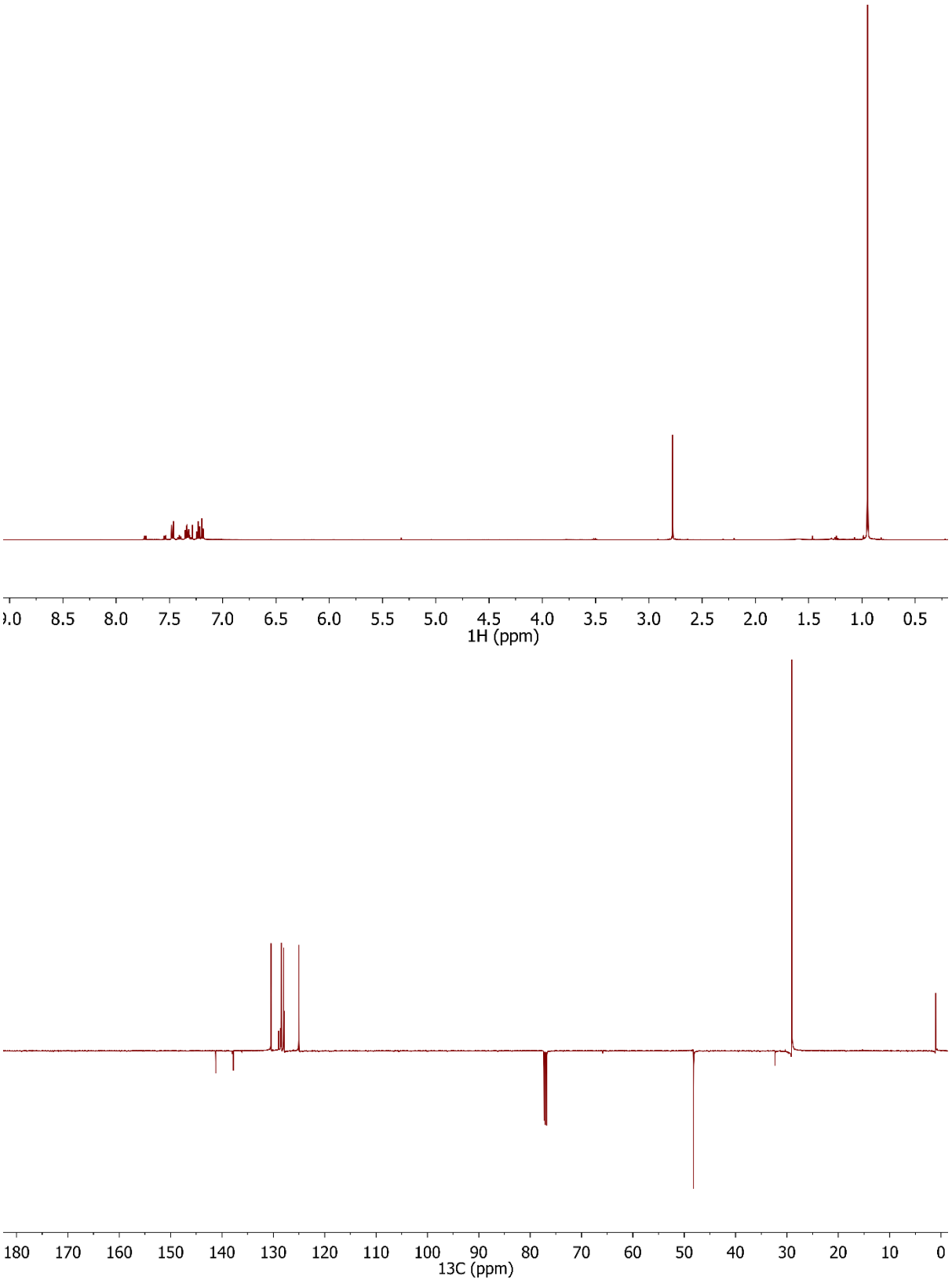
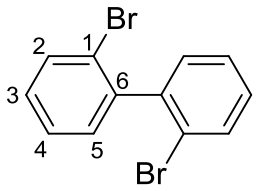


Figure S9: ^{1}H (500.1 MHz, $CDCl_3$, 295 K) (top) and $^{13}C\{^{1}H\}$ DEPT-Q (125.8 MHz, $CDCl_3$, 295 K) (bottom) NMR spectra for compound **10**.

2. Synthetic Methods

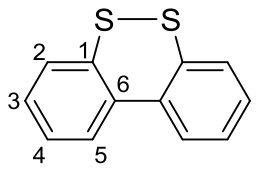
2.1 Synthesis of 2,2'-dibromobiphenyl (1)



Prepared following the literature procedure.[1]

To a solution of 1,2-dibromobenzene (2.03 g, 8.61 mmol) in dry THF (25 mL) cooled to −78 °C, a solution of *n*-BuLi (1.7 mL, 2.5 M in hexane, 4.25 mmol) was added dropwise over a 15 minute period. The flask was then stirred at −78 °C for an hour, then warmed to room temperature and stirred overnight. After quenching the reaction with distilled water (30 mL), the product was extracted using diethyl ether (3 x 20 mL). After combining and drying the organic layers over magnesium sulfate, the solvent was removed *in vacuo* to yield the product as a pale yellow liquid, which solidified into a pale yellow solid (1.03 g, 6.37 mmol, 74%), m.p 79-81 °C (lit. 79-80 °C).[2] ^{1}H NMR: δ_H (270.1 MHz, $CDCl_3$) 7.71 (2H, d, $^{3}J_{HH}$ 7.5 Hz, H-2), 7.42 (2H, *pseudo*-td, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.1 Hz, H-4), 7.32-7.28 (4H, m, H-3,5). ^{13}C NMR: δ_C (125.8 MHz, $CDCl_3$) 141.9 (ArC_q, C-6), 132.4 (ArCH, C-2), 130.8 (ArCH, C-5), 129.3 (ArCH, C-3), 126.9 (ArCH, C-4), 123.4 (ArC_q, C-1). IR (KBr): ν_{max}/cm^{-1} 3055w (ν_{Ar-H}), 1455m, 1454m, 1423m, 1025s, 1002m, 760s (ν_{C-Br}). Raman (glass capillary): ν_{max}/cm^{-1} 3054m (ν_{Ar-H}), 1597s, 1027s, 654m (ν_{C-Br}), 388s.

2.2 Synthesis of dibenzo[*c,e*][1,2]dithiin (2)

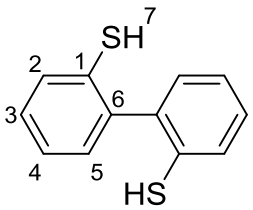


Prepared following a procedure described for the synthesis of naphtho[1,8-cd]-1,2-dithiole.[3]

To a solution of biphenyl (5.01 g, 32.4 mmol) in hexane (25 mL), TMEDA (9.7 mL, 64.8 mmol) and *n*-BuLi (25.9 mL, 2.5M in hexane, 64.8 mmol) were added. The solution was heated to 60 °C, and stirred for three hours. The resulting suspension was cooled to −78 °C, before being diluted with dry THF (20 mL). Sulfur (3.04 g, 94.7 mmol) was added and the reaction mixture was stirred overnight at room temperature. The mixture was washed with water until the aqueous layer remained

colourless. The organic layer was dried over magnesium sulfate before the solvent was removed *in vacuo,* affording a crude yellow solid. Purification using column chromatography yielded the pure yellow product (2.86 g, 13.2 mmol, 41%), m.p 113-114 °C (lit. 113 °C).[4] ^{1}H NMR: δ_H (270.1 MHz, $CDCl_3$) 7.69 (4H, dd, $^{3}J_{HH}$ 7.8, $^{4}J_{HH}$ 1.5 Hz, H-5), 7.51 (2H, d, $^{3}J_{HH}$ 7.6 $^{4}J_{HH}$ 1.5 Hz, H-2), 7.37 (2H, *pseudo*-td, $^{3}J_{HH}$ 7.6, $^{4}J_{HH}$ 1.5 Hz, H-4), 7.28 (2H, *pseudo*-td, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.5 Hz, H-3). ^{13}C NMR: δ_c (125.8 MHz, $CDCl_3$) 138.0 (ArC_q, C-6), 136.1 (ArC_q, C-1), 129.0 (ArCH, C-2), 128.6 (ArCH, C-4), 127.9 (ArCH, C-3,5). IR (KBr): ν_{max}/cm^{-1} 3057w (ν_{Ar-H}), 2362m, 1455m, 1417m, 751s (ν_{C-S}). Raman (glass capillary): ν_{max}/cm^{-1} 3059m (ν_{Ar-H}), 1583s, 1298m, 1041s, 524s (ν_{C-S}), 437m (ν_{S-S}).

2.3 Synthesis of 1,1'-biphenyl-2,2'-dithiol (3)



Prepared following a procedure described for the synthesis of 1,8-naphthalenedithiol.[5]

To a solution of $NaBH_4$ (1.32 g, mmol) in ethanol (30 mL) stirred at 0°C, a solution of **4** (2.51 g, 11.6 mmol) in THF (25 mL) was added dropwise. After all of the dithiin solution was added, the mixture was stirred for 15 minutes and the resulting solution was poured into water (30 mL). A 3M solution of HCl was added to acidify the reaction, before the product was extracted using diethyl ether (3 x 40 mL). The organic layer was dried over magnesium sulfate. Removal of the solvent under reduced pressure yielded a white solid (2.31 g, 10.6 mmol, 91%), m.p 78-79 °C (lit. 78-79 °C).[6] ^{1}H NMR: δ_H (270.1 MHz, $CDCl_3$) 7.44 (2 H, dd, $^{3}J_{HH}$ 7.7, $^{4}J_{HH}$ 1.3 Hz, 5-H), 7.27 (2 H, *pseudo*-td, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.5 Hz, 4-H), 7.23 (2 H, *pseudo*-td, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.5 Hz, 3-H), 7.16 (2 H, td, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.5 Hz, 2-H), 3.29 (2 H, s, 7-H). ^{13}C NMR: δ_c (125.8 MHz, $CDCl_3$) 139.0 (ArC_q, C-6), 131.8 (ArC_q, C-1), 130.3 (ArCH, C-2), 129.4 (ArCH, C-5), 128.7 (ArCH, C-4), 125.8 (ArCH, C-3). IR (KBr): ν_{max}/cm^{-1} 3127w (ν_{Ar-H}), 2559m (ν_{S-H}), 1455s, 1426s, 1071m, 753s (ν_{C-S}), 731m. Raman (glass capillary): ν_{max}/cm^{-1} 3055m (ν_{Ar-H}), 2561s (ν_{S-H}), 1590m, 1296m, 1246m, 1038s, 669m (ν_{C-S}).

3. Calculations for AB quartets

3.1 Calculation of the true centres of the AB quartet in 4

$|J_{AB}|$ = ($\nu_1 - \nu_2$) = ($\nu_3 - \nu_4$) = 12.903 Hz

ν_{centre} = ½ ($\nu_2 + \nu_3$) = 1596.30155 Hz

$\nu_{AB} = \sqrt{(\nu 1 - \nu 4)(\nu 2 - \nu 3)}$

$= \sqrt{(32.3082)(6.5025)}$

$=\sqrt{210.084}$

= 14.494 Hz

Therefore ½ ν_{AB} = 7.247 Hz

$\nu_A = \nu_{centre} + ½\ \nu_{AB}$ = 1603.548689 Hz = **4.01 ppm** (@ 400.1 MHz)

$\nu_B = \nu_{centre} - ½\ \nu_{AB}$ = 1589.05455 Hz = **3.97 ppm** (@ 400.1 MHz)

3.2 Calculation of the true centres of the AB quartet in 5

$|J_{AB}|$ = ($\nu_1 - \nu_2$) = ($\nu_3 - \nu_4$) = 12.7975 Hz

ν_{centre} = ½ ($\nu_2 + \nu_3$) = 1988.3022 Hz

$\nu_{AB} = \sqrt{(\nu 1 - \nu 4)(\nu 2 - \nu 3)}$

$= \sqrt{(34.4506)(8.8556)}$

$=\sqrt{305.0807}$

= 17.46656 Hz

Therefore ½ ν_{AB} = 8.73328Hz

$\nu_A = \nu_{centre} + ½\ \nu_{AB}$ = 1997.03548 Hz = **4.00 ppm** (@ 500.1 MHz)

$\nu_B = \nu_{centre} - ½\ \nu_{AB}$ = 1979.56892 Hz = **3.96 ppm** (@ 500.1 MHz)

3.3 Calculation of the true centre of the AB quartet in 6

$|J_{AB}|$ = ($\nu_1 - \nu_2$) = ($\nu_3 - \nu_4$) = 13.2687 Hz

ν_{centre} = ½ ($\nu_2 + \nu_3$) = 1939.51 Hz

$\nu_{AB} = \sqrt{(\nu 1 - \nu 4)(\nu 2 - \nu 3)}$

$= \sqrt{(32.1791)(5.6417)}$

$=\sqrt{181.5448}$

= 13.4792 Hz

Therefore ½ ν_{AB} = 6.7369 Hz

$\nu_A = \nu_{centre} + ½\ \nu_{AB}$ = 1943.2469 Hz = **3.89 ppm** (@ 500.1 MHz)

$\nu_B = \nu_{centre} - ½\ \nu_{AB}$ = 1937.7731 Hz = **3.85 ppm** (@ 500.1 MHz)

3.4 Calculation of the true centre of the AB quartet in 7

$|J_{AB}| = (\nu_1 - \nu_2) = (\nu_3 - \nu_4)$ = 13.0621 Hz

$\nu_{centre} = ½\ (\nu_2 + \nu_3)$ = 1962.3710 Hz

$\nu_{AB} = \sqrt{(\nu 1 - \nu 4)(\nu 2 - \nu 3)}$

$= \sqrt{(33.75)(7.6217)}$

$= \sqrt{257.2011}$

= 16.0345 Hz

Therefore ½ ν_{AB} = 8.0187 Hz

$\nu_A = \nu_{centre} + ½\ \nu_{AB}$ = 1970.39 Hz = **3.95 ppm** (@ 500.1 MHz)

$\nu_B = \nu_{centre} - ½\ \nu_{AB}$ = 1954.35 Hz = **3.91 ppm** (@ 500.1 MHz)

3.5 Calculation of the true centre of the AB quartet in 8

$|J_{AB}| = (\nu_1 - \nu_2) = (\nu_3 - \nu_4)$ = 13.3944 Hz

$\nu_{centre} = ½\ (\nu_2 + \nu_3)$ = 1581.6255 Hz

$\nu_{AB} = \sqrt{(\nu 1 - \nu 4)(\nu 2 - \nu 3)}$

$= \sqrt{(29.66)(1.87)}$

$= \sqrt{55.4554}$

= 7.4468 Hz

Therefore ½ ν_{AB} = 3.72 Hz

$\nu_A = \nu_{centre} + ½\ \nu_{AB}$ = 1585.3455 Hz = **3.96 ppm** (@ 400.1 MHz)

$\nu_B = \nu_{centre} - ½\ \nu_{AB}$ = 1577.9055 Hz = **3.94 ppm** (@ 400.1 MHz)

3.6 Calculation of the true centre of the AB quartet in 9

$|J_{AB}| = (\nu_1 - \nu_2) = (\nu_3 - \nu_4)$ = 13.6401 Hz

$\nu_{centre} = ½\ (\nu_2 + \nu_3)$ = 1985.56Hz

$\nu_{AB} = \sqrt{(\nu 1 - \nu 4)(\nu 2 - \nu 3)}$

$= \sqrt{(34.79)(7.51)}$

$=\sqrt{261.2729}$

= 16.1639 Hz

Therefore ½ ν_{AB} = 8.08 Hz

$\nu_A = \nu_{centre} + ½\ \nu_{AB}$ = 1993.64 Hz = **3.99 ppm** (@ 500.1 MHz)

$\nu_B = \nu_{centre} - ½\ \nu_{AB}$ = 1977.48 Hz = **3.95 ppm** (@ 500.1 MHz)

4. References

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[5] K. Yui, Y. Aso, T. Otsubo, F. Ogura, Syntheses and Properties of 2,2'-Binaphtho[1,8-De]-1,3-Dithiinylidene and Its Selenium Analog, 2-(1,3-Dithiol-2-Ylidene)Naphtho[1,8-De]-1,3-Dithiin, and 2-(4h-Thiopyran-4-Ylidene)Naphtho[1,8-De]-1,3-Dithiin, Bull. Chem. Soc. Jpn. 61(3) (1988) 953-959.

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